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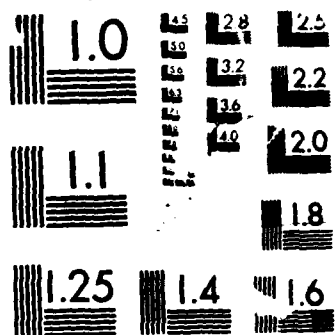
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# SYNTHESIS OF POLYNITROCUBANES

October 1987

Annual Report

By:

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- (b) Cubane-1,4-bis(trinitroethylester)
  - (c) Bis(N,N'-fluorodinitroethyl)-1,4-diaminocubane
  - (d) N-Nitro-N'-nitroso-N,N'-fluorodinitroethyl-1,4-diaminocubane
- (2) We have started the synthesis of other tetrasubstituted energetic cubanes:
- (a) Cubane-1,2,4,7-tetrakis(trinitroethylester)
  - (b) 1,2,4,7-tetracyanocubane
- (3) Several advances in cubane methodology have been made.
- (a) Development of new, easily removable cubylamides,  $C(O)TMP$  and  $C(O)NHC(CH_3)_3$
  - (b) Synthesis of  $Si(CH_3)_3$  substituted cubanes by reverse metallation reactions
  - (c) An exploration of the possibilities of cubane acylation using intra or intermolecular acylating agents.

To meet the ultimate goal of synthesis of polynitrocubanes, we are also proceeding with our studies on direct nitration of the cubyl ring system.

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## SUMMARY

The objective of this research is to prepare polynitrocubanes for possible application as either explosives or propellants. During this reporting period, we have explored the synthesis of fluorodinitroethyl and trinitroethyl substituted cubane esters and amines. This work has led to the synthesis of the first cubane with more than two nitro groups. One of the highlights of this research is the synthesis of tetrakis(fluorodinitroethyl)-1,2,4,7-cubane-tetracarboxylate, the first cubane explosive that is balanced to CO, H<sub>2</sub>O, N<sub>2</sub>, and HF. This is an exciting advance because tetrakis(fluorodinitroethyl)-1,2,4,7-cubane-tetracarboxylate is quite thermally stable. A second interesting cubane is N-nitro-N'-nitroso-bis(N,N'-fluorodinitroethyl)-1,4-diaminocubane, a very interesting derivative of diamino-cubane that will be discussed later in this report.

In summary, our work over the past year has resulted in the following accomplishments:

- (1) Synthesis of several highly nitrated cubanes.
  - (a) Cubane-1,2,4,7-tetrakis(fluorodinitroethylester)
  - (b) Cubane-1,4-bis(trinitroethylester)
  - (c) Bis(N,N'-fluorodinitroethyl)-1,4-diaminocubane
  - (d) N-Nitro-N'-nitroso-N,N'-fluorodinitroethyl-1,4-diaminocubane
- (2) We have started the synthesis of other tetrasubstituted energetic cubanes.
  - (a) Cubane-1,2,4,7-tetrakis(trinitroethylester)
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- (3) Several advances in cubane methodology have been made.
  - (a) Development of new, easily removable cubylamides, C(O)TMP and C(O)NHC(CH<sub>3</sub>)<sub>3</sub>
  - (b) Synthesis of Si(CH<sub>3</sub>)<sub>3</sub> substituted cubanes by reverse metallation reactions
  - (c) An exploration of the possibilities of cubane acylation using intra or intermolecular acylating agents

To meet the ultimate goal of synthesis of polynitrocubanes, we are also proceeding with our studies on direct nitration of the cubyl ring system.

## INTRODUCTION

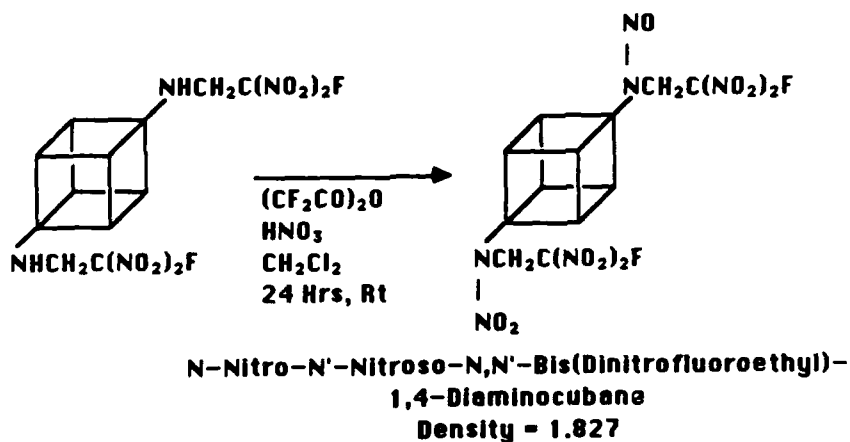
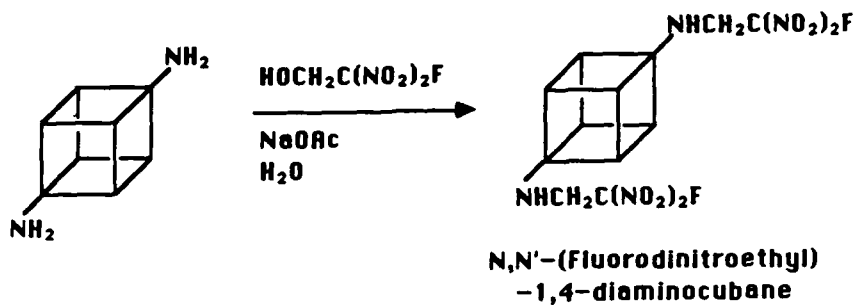
The need to pack more power into weapons of the future has lead to this program for the synthesis of highly energetic materials based on the cubane nucleus. Cubane is a dense ( $r = 1.29$  g/cc), highly strained hydrocarbon (strain energy = +166 kcal/mole,  $\Delta H_f = +144$  kcal/mole) to which energetic groups can be added to create exceptionally dense and powerful explosives, propellants, and fuels. Thus, the incorporation of a cubane nucleus will greatly enhance the performance of any explosive or propellant molecule. For example, one part of our program is devoted to developing methods to synthesize cubane explosives with four to eight nitro groups on the cubane nucleus. Based on theoretical calculations, octanitrocubane should be a radical improvement over currently available propellant/explosive materials. Tremendous progress has been made in polyfunctionalization of the cubane nucleus, and we are applying this chemistry to the synthesis of nitrated cubanes.

## RESULTS

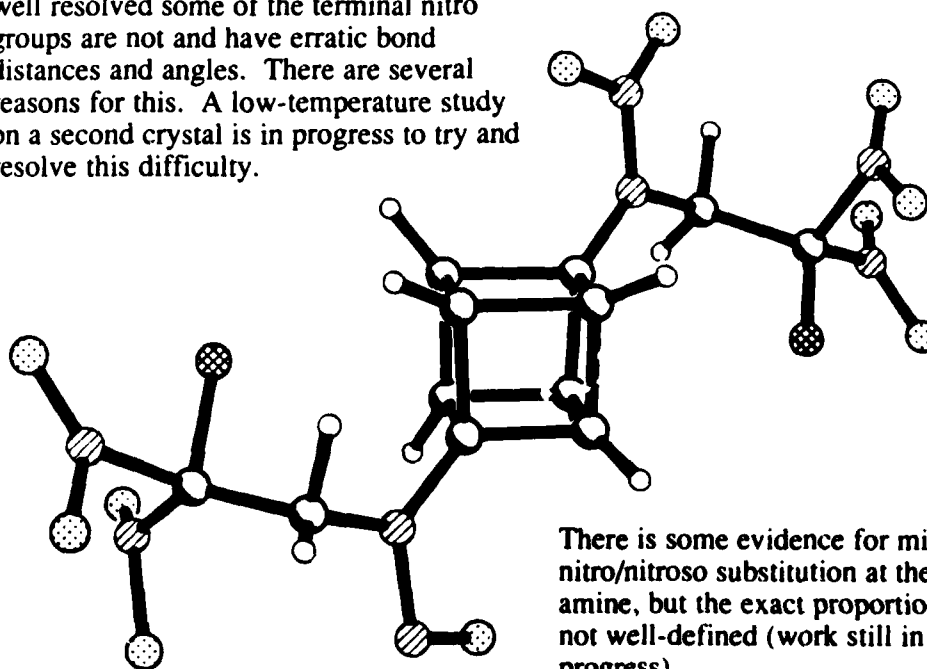
### Polynitro Derivatives of Amino Cubane

We have succeeded in synthesizing the first polynitro cubane compounds. The derivatives we prepared have fluorodinitromethyl groups substituted at the amino group of a cubane. Clearly, these compounds are only intermediate targets along the pathway to the synthesis of cubanes that are nitrated on the cage. We have prepared two amino-substituted cubanes; first, bis-(N,N'-fluorodinitroethyl)-1,4-diaminocubane, which was then further nitrated to give N-nitro-N'-nitroso-bis(N,N'-fluorodinitroethyl)-1,4-diaminocubane.



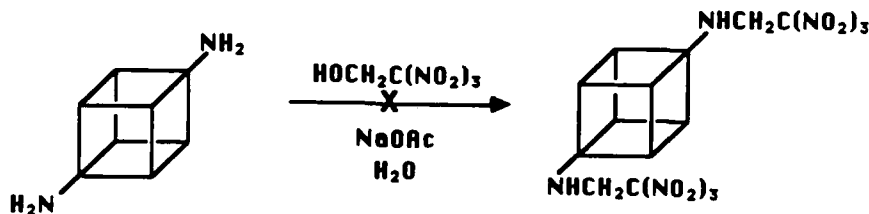


While the cubane and chain backbones are well resolved some of the terminal nitro groups are not and have erratic bond distances and angles. There are several reasons for this. A low-temperature study on a second crystal is in progress to try and resolve this difficulty.



One remarkable aspect of the synthesis is that the stability of N-nitro-N'-nitroso-N,N'-fluorodinitroethyl-1,4-diaminocubane is considerably greater than that for N,N'-fluorodinitroethyl-1,4-diaminocubane. It has been observed that the amino-cubane system is unstable, eventually decomposing via opening of the cubane ring system. The N-nitro groups stabilize the amino-cubane system by withdrawing electron density from the amino group, preventing donation of the lone pair of electrons on the amino group from being back donated into the cage and catalyzing its decomposition. This is an important observation, because it indicates that nitrocubanes or amino-cubanes with strongly electron-withdrawing groups will be stable.

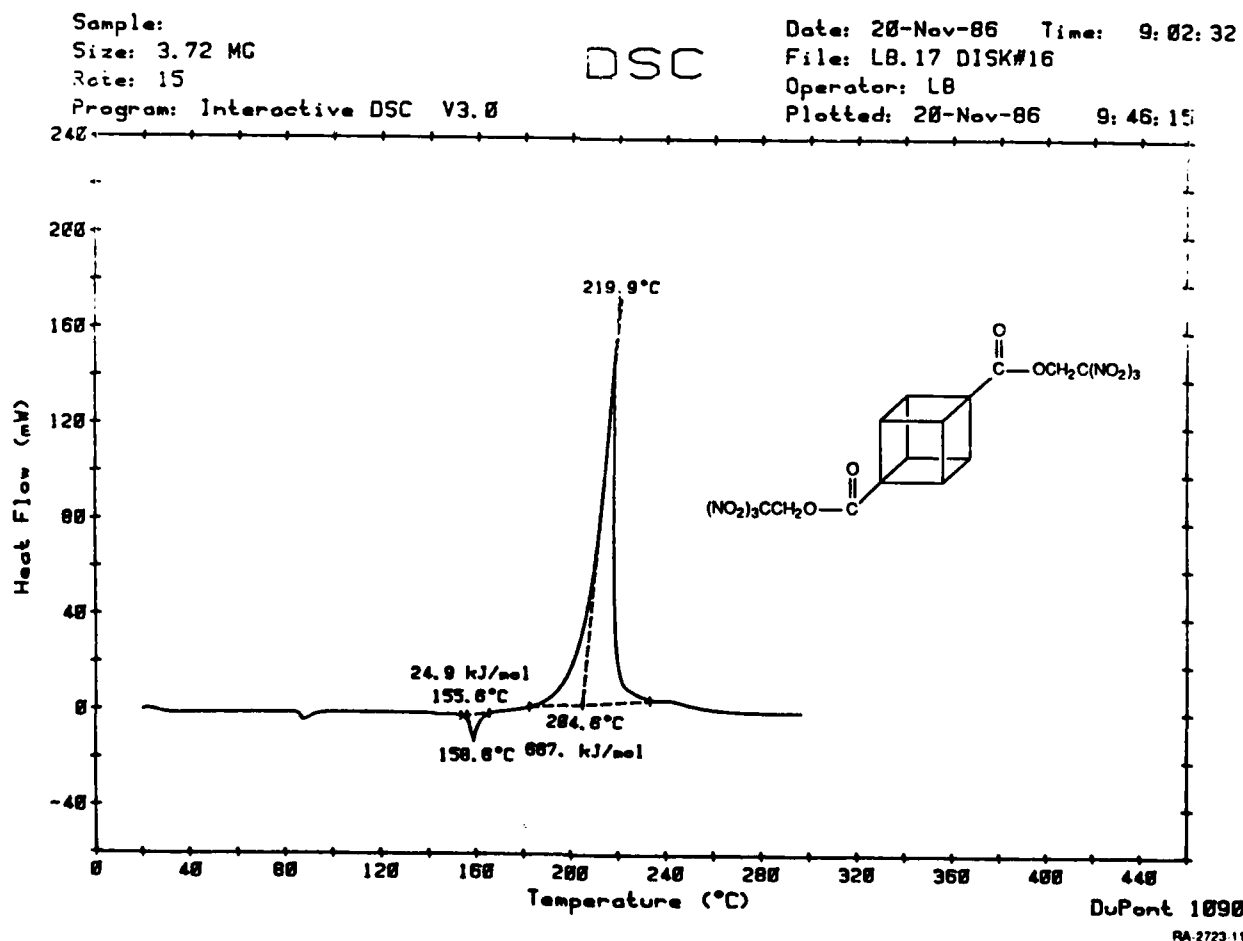
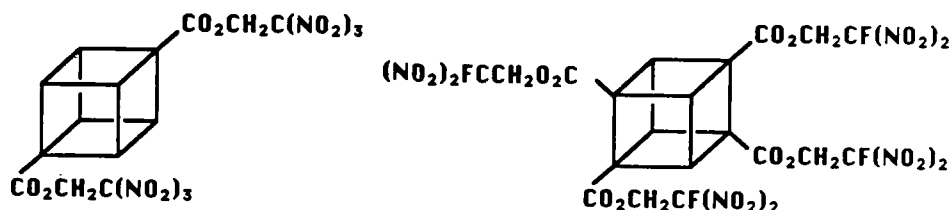
We also attempted the synthesis of the analogous N,N'-trinitroethyl-1,4-diaminocubane. This compound is of interest because of its considerably higher heat of formation and oxygen density. However, no attempts to synthesize this material have yet succeeded. From all results, the  $\text{NHCH}_2\text{C}(\text{NO}_2)_3$  group on a cubane is not stable and ionization to the trinitromethide salt ( $-\text{NH}_3^+\text{C}(\text{NO}_2)_3^-$ ) dominates.



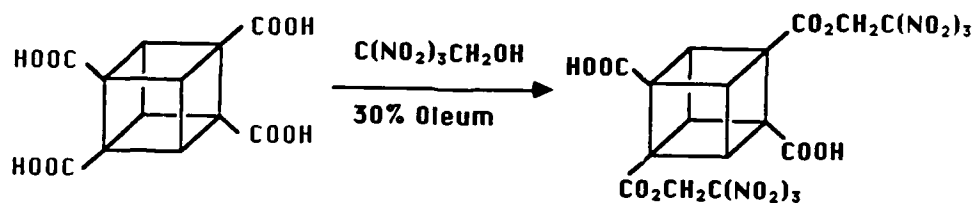
#### Esters of Trinitroethanol and Fluorodinitroethanol

We have also prepared cubane esters substituted with trinitroethanol (TNE) and fluorodinitroethanol (FDNE). These compounds give immediate access into very highly nitrated cubanes. To date, we have synthesized two esters, cubane-1,4-bis(trinitroethylester) and cubane-1,2,4,7-tetrakis(fluorodinitroethylester). Structures of the compounds synthesized are shown below. Cubane-1,2,4,7-tetrakis(fluorodinitroethylester)

represents the first example of an energetic material balanced to CO or greater that has been made from a cubane nucleus. Dr. Richard Gilardi of the Naval Research Laboratory has done on X-ray crystal structure of cubane-1,2,4,7-tetrakis(fluorodinitroethylester) to confirm our structure for the molecule. He obtained from the crystal structure a density of  $1.762 \text{ g/cm}^3$ . We have also attached the DSCs of both cubane-1,2,4,7-tetrakis(fluorodinitroethylester) compounds and cubane-1,4-bis(trinitroethylester) as well as the X-ray crystal structure for cubane-1,2,4,7-tetrakis(fluorodinitroethylester).



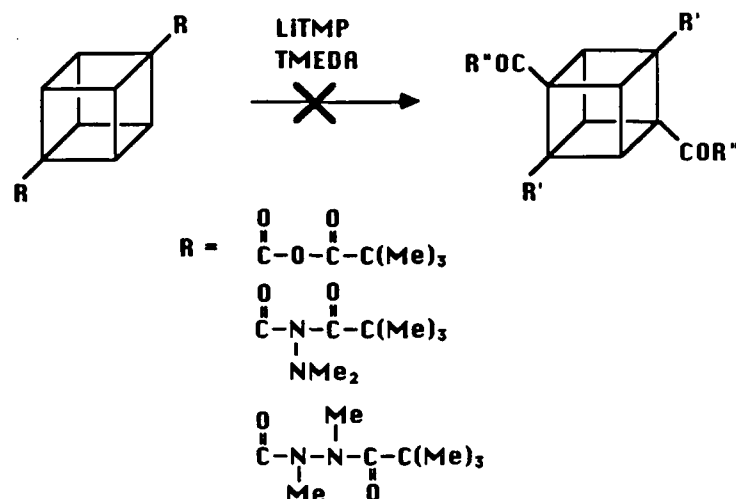
Earlier in the year, we believed that we had synthesized cubane-1,2,4,7-tetrakis(trinitroethylester). After subsequent analysis, this proved not to be the case. However, we are still working on the synthesis of this compound and have made some progress toward this goal. We have just finished the synthesis of cubane-1,2,4,7-tetraacid-1,4-bis(trinitroethylester) under very interesting conditions. We treated cubane-1,2,4,7-tetraacid with 30% oleum and trinitroethanol for three days, isolating only cubane-1,2,4,7-tetraacid-1,4-bis(trinitroethylester).



We have not yet been able to isolate cubane-1,2,4,7-tetrakis(trinitroethylester), but we believe that this approach or an improvement in one of our earlier methods will result in the synthesis of this desired compound.

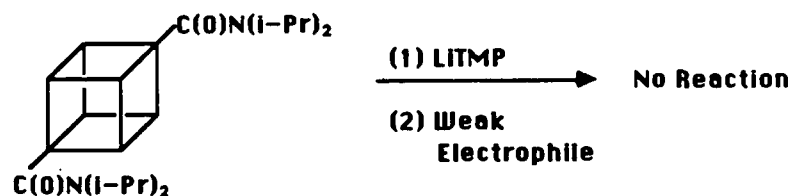
#### Inter and Intramolecular Acylations

We expended a great deal of effort over the past year on methods to directly transfer a group from a side chain on the cubane, to the cubane nucleus after treatment with strong base. We reasoned that several steps could be eliminated in the synthesis if this methodology were successful. Two different approaches were taken. The first involved the synthesis of a cubyl system substituted with a functional group that is stable to LiTMP, yet would be expected to react with the cubyl anion in an intramolecular reaction. Several different side chain groups were tried, as shown in the equation below.



All attempts at intramolecular acylations have thus far failed. We believe that this failure is due to a combination of the very slow rate of proton abstraction from cubane by LiTMP coupled with a fairly short lifetime for the existence of the cubyl anion and, more importantly, a slow proton abstraction reaction by LiTMP on the side chains despite their lack of acidic protons. Work by Eaton has shown that cubyl anions will react with metals or organometallics such as  $\text{HgCl}_2$ ,  $\text{Si}(\text{CH}_3)_3\text{Cl}$ , or  $\text{Sn}(\text{CH}_3)_3\text{Cl}$  to metallate the cubane ring in the presence of LiTMP. This approach should also work to add a carboxylic acid or a carboxylic acid equivalent if the appropriate acyl equivalents are chosen.

Following the above reasoning, we tried several different acyl equivalents in an attempt to directly add a carbonyl group to cubane.

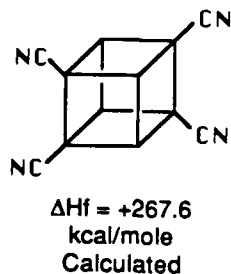
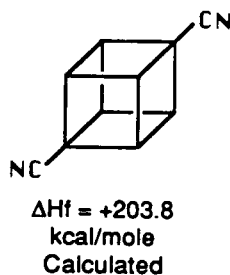


Electrophile =  $t\text{-Butyl-N}^+\text{C}^-$   
 $n\text{-Butyl-O-C(O)-O}^-$   
 $\text{C(OMe)}_4$   
 $n\text{-Propyl-S-CH}_2\text{-N(CH}_3)_2$

Unfortunately, all these attempts at intramolecular functionalization have thus far failed. We have not yet given up on this approach because it potentially represents the easiest and most direct way to prepare polyfunctional cubanes. Over the next year, we will attempt to find an acylating agent that will work in this environment to give us the desired product.

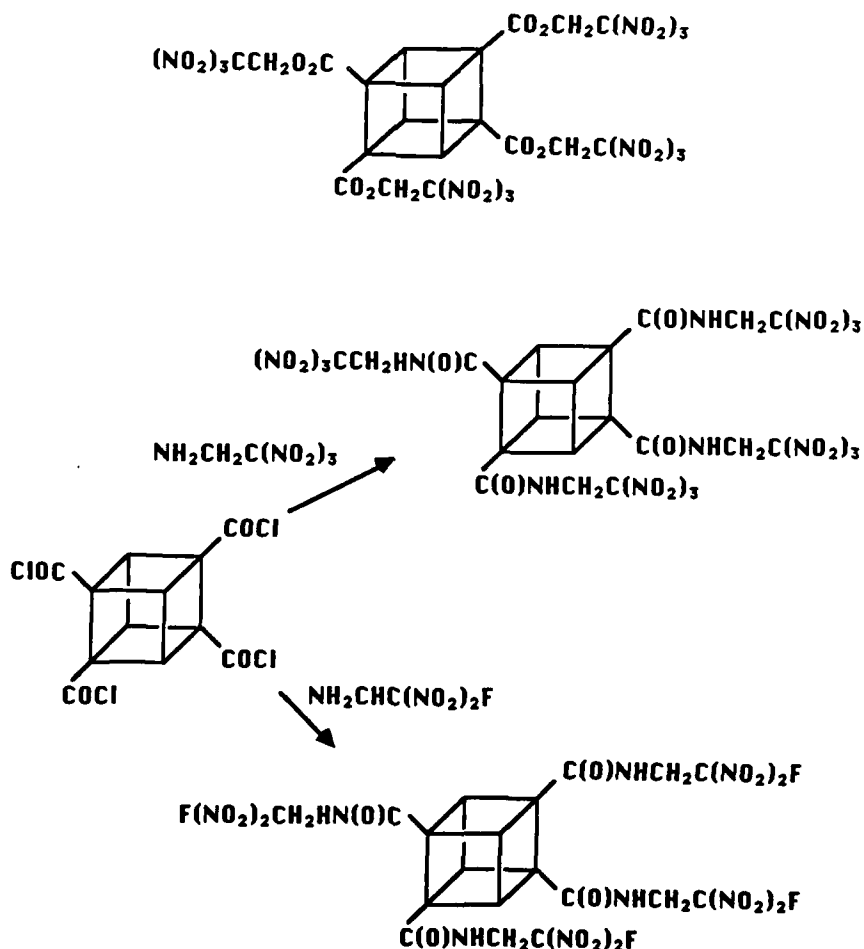
#### Polycyanocubanes

We have started work on the synthesis of polycyanocubanes for use as dense, high energy rocket fuels. For example, octacyanocubane is calculated to have a  $\Delta H_f$  of +395 kcal/mole and a density greater than 1.5 g/cc. Thus, these cyanocubanes would be ideal energy dense fuels for volume limited applications. We also have synthesized 1,4-dicyanocubane and are currently attempting to synthesize tetracyanocubane as an example of these compounds. Tetracyanocubane is calculated to have a  $\Delta H_f$  of +267 kcal/mole and its synthesis presents no special challenges. We will prepare the rest of the cyanocubanes as we proceed in this program.

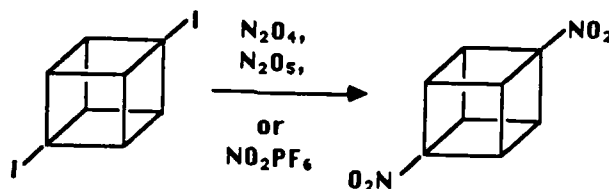


# RESEARCH PLANS FOR NEXT YEAR

Over the next year, we will first complete the synthesis of cubane-1,2,4,7-tetra(trinitroethylester). Following this we will synthesize cubane-1,2,4,7-tetra(trinitroethylamide) and cubane-1,2,4,7-tetra-(fluorodinitroethylamide). The tetra(trinitroethyl)amide will have a significantly higher heat of formation than the tetraester and probably a higher density as well. These two materials represent excellent examples of very highly nitrated cubanes, which should have value as energetic materials.



Next, we will concentrate our efforts on the synthesis of cubanes that are nitrated directly on the cubane ring system. All calculations show that these directly nitrated cubanes have the greatest promise of any of the polynitrocubanes as energetic materials. Our studies on this system will begin with attempts to convert cubyl-iodides first to the hypervalent iodine compound and then to the corresponding nitro compound. Several methods are currently being examined using the 1,4-diiodocubane as a model system involving oxidation by  $N_2O_4$ ,  $N_2O_5$ , or  $NO_2PF_6$ .



If this approach should succeed, we will apply this chemistry to the synthesis of 1,2,4,7-tetranitrocubane. Alternatively, should these initial attempts fail, we will explore a number of other oxidants for the iodocubanes. The next approach to the synthesis of nitrocubanes will involve attempts at direct nitrodemetallation of the cubyl ring system. Here, we will concentrate on the replacement of silyl or stannyl groups by direct nitrodemetallation reactions. We have not yet concentrated on this chemistry to follow up other, promising leads, but this still represents a viable route to the synthesis of nitrocubanes.

#### CONCLUSIONS

In summary, we have synthesized several polysubstituted cubanes as well as several members of a new class of energetic, high density fuels. We are now prepared for a major effort toward the synthesis of the highest energy cubanes where the nitro group is directly attached to the cage, such as tetranitrocubane and beyond.



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